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The Formation of $SrFe_{12}O_{19}$ in the Presence of $Fe(OH)_2$

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Alkaline suspensions containing Sr(II), either $FeCl_2$ or $FeSO_4$, and different concentrations of excess NaOH and $NaNO_3$ were subjected to autoclaving at temperatures between 180 and 300°C. Ferromagnetic platelike $SrFe_{12}O_{19}$ particles were formed with or without α-Fe_2O_3 ones in the presence of $Sr(OH)_2$ and iron(II) hydroxide with the 1 : 4 atomic ratio under the conditions where the transformation into α-Fe_2O_3 proceeded. The presence of sulfates in the starting suspensions facilitated the $SrFe_{12}O_{19}$ formation. The magnetic properties of the $SrFe_{12}O_{19}$ samples were investigated at room temperature.

KEY WORDS: $Fe(OH)_2$/ α-Fe_2O_3/ $NaNO_3$/ $SrFe_{12}O_{19}$/ Ferromagnetic precipitate/ Coercivity/ Autoclaving/ Alkaline Suspension

INTRODUCTION

Strontium Ferrite $SrFe_{12}O_{19}$, one of the M-type hexagonal ferrites, can be obtained by a solid state reaction between iron oxide and strontium carbonate. Its properties have been well investigated and it is widely used as economical permanent magnets.[1] A precipitate of $SrFe_{12}O_{19}$ could be prepared at temperatures below 300°C in the presence of $Sr(OH)_2$ and iron (III) hydroxide with the 1 : 4 atomic ratio under the conditions where the transformation into α-Fe_2O_3 proceeded.[2] A nonferromagnetic precipitate, $Sr_3Fe_2(OH)_{12}$, was formed at the $Sr(OH)_2$ concentration higher than that for the $SrFe_{12}O_{19}$ formation.[3)4)] The $SrFe_{12}O_{19}$ formation was hindered in the presence of a slight amount of carbonates, which are formed from CO_2 in the atmosphere in the starting, alkaline suspension, but facilitated in the presence of sulfates.[2] It was reported that the addition of nitrates enables the use of Fe(II) as the source of Fe(III) in forming α-Fe_2O_3 or $BaFe_{12}O_{19}$ particles.[5]

We also succeeded in preparing $SrFe_{12}O_{19}$ in the absence or presence of sulfates by autoclaving alkaline suspensions containing $Fe(OH)_2$, $Sr(OH)_2$, and $NaNO_3$. This paper describes the conditions for the formation of $SrFe_{12}O_{19}$ from $Fe(OH)_2$ and the magnetic properties at room temperature for the samples obtained in this work.

EXPERIMENTAL

Acidic solutions containing Fe(II) and Sr(II) in a 4 : 1 atomic ratio and different concentrations of excess NaOH and nitrates were preparaed in a 1 dm^3 autoclave made of

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stainless steel, by mixing aqueous solutions of either strontium nitrate or chloride, either iron (II) chloride or sulfate, and sodium nitrate (each of reagent grade). To this an excess of NaOH solution was added in a required amount and each resulting suspension was diluted with conductivity water to 0.7 dm^3.

A number of alkaline suspensions, each containing 0.45 M (M=mol/dm^3) Fe(II) and 0.11 M Sr(II), were prepared by varying the concentrations of excess NaOH, and nitrates, under the condition where great care had been taken to exclude the formation of $SrCO_3$ with CO_2 from the atmosphere. They were heated to desired temperatures at a rate of 4°C/min and kept at 180, 200, 250, or 300°C with mechanical stirring at 750 rpm for a fixed time of 5h and then allowed to cool to room remperature. The resulting products were separated by filtration, treated with 1 M HCl to remove remaining Sr(II) as carbonate, well washed with water, and then dried at 80°C in air. The products prepared in the presence of sulfates were treated with a sodium carbonate solution to transform remaining $SrSO_4$ into carbonate before the acid treatment.

The products were subjected to examinations by X-ray diffraction using Fe$K\alpha$ radiation (XRD) and scanning electron microscopic observation (SEM). Magnetic measurements on the ferromagnetic samples were carried out at room temperature in a magnetic field up to 10 kOe (1 kOe=$10^6/4\pi Am^{-1}$), using a vibrating-sample magnetometer.

RESULTS AND DISCUSSION

The starting, alkaline suspensions containing 0.45 M $FeCl_2$, 0.11 M $Sr(NO_3)_2$, 0.15 M $NaNO_3$ and one of 0.1, 0.3 or 0.6 M excess NaOH were subjected to autoclaving at temperatures between 180 and 300°C. Ferromagnetic, brownish precipitates, consisting of $SrFe_{12}O_{19}$ with α-Fe_2O_3, were formed in the presence of 0.37 M total nitrates at temperatures above 200°C, the $SrFe_{12}O_{19}$ content depending on the concentration of excess NaOH. On the other hand, Fe_3O_4 particles were formed with a slight amount of α-FeO(OH) at 180°C in the presence of 0.6 M excess NaOH. The properties of typical samples consisting of $SrFe_{12}O_{19}$ with different amounts of α-Fe_2O_3 are given in Table 1. The values of magnetization at 10 kOe, M, (1 emu/g=$4\pi\rho$ 10^{-4}T, where ρ=5.0 is specific gravity) increased with increasing the $SrFe_{12}O_{19}$ content, and those of coercive force, Hc, did not depend strongly on the conditions for their formation.

In order to investigate the effect of the concentration of the total nitrates on the $SrFe_{12}O_{19}$ content, alkaline suspensions containing 0.6 M excess NaOH, $FeCl_2$ and $SrCl_2$ and one of 0.15,

Table 1. Properties of the Typical Samples Prepared by Autoclaving at Different Temperatures, T, of Aqueous Suspensions Containing 0.45M $FeCl_2$, 0.15 M $NaNO_3$, 0.11 M $Sr(NO_3)_2$ and One of 0.1, 0.3 or 0.6 M Excess NaOH.

Sample	Excess NaOH/M	T/°C	M/emu g^{-1}	Hc/kOe
A1	0.1	300	27	0.8
A2	0.3	300	46	0.9
A3	0.6	300	47	0.6
A4	0.6	250	46	0.7
A5	0.6	300	46	0.9

Table 2. Effect of the Total Nitrate Concentration on the $SrFe_{12}O_{19}$ Formation in the Presence of 0.6 M Excess NaOH.

Sample	Nitrates /M	T/°C	M/emu g^{-1}	Hc/kOe
B1	0.15	300	48	0.6
B2	0.45	300	48	0.7
B3	0.15	200	39	0.7
B4	0.45	200	51	0.6
B5	1.0	200	49	0.9

0.45, or 1.0 M $NaNO_3$ were subjected to autoclaving at 200 or 300°C. The nitrate concentration required for the formation of $SrFe_{12}O_{19}$ became smaller with an increase in the temperature (Table 2).

When similar experiments were carried out with iron(II) sulfate in place of the chloride, a marked difference was found in the concentration of excess NaOH required for the satisfactory $SrFe_{12}O_{19}$ content in the products. Experiments were conducted by using the alkaline suspensions containing $FeSO_4$, $Sr(NO_3)_2$, 0.15 M $NaNO_3$ and different concentrations of excess NaOH. The starting suspensions with 0.37 M in the total nitrate concentration were subjected to autoclaving at 200, 250 or 300°C. Extensive experiment by varying the concentration of excess NaOH demonstrated that the products, which were obtained without treatment with sodium carbonate solution before the acid treatment, were found by XRD to consist of $SrFe_{12}O_{19}$ and slight amounts of either a mixture of $SrSO_4$ and α-Fe_2O_3, or α-Fe_2O_3 and that the content of the mixture of $SrSO_4$ and α-Fe_2O_3 in the products decreased with increasing the concentration of excess NaOH to 3 M. A further increase in the NaOH concentration from 4 M retarded the formation of $SrFe_{12}O_{19}$, probably because of an increase in the amount of $SrCO_3$ formed with CO_2 from the atmosphere in the starting, strongly alkaline suspension. The properties of some typical samples are given in Table 3.

In order to examine also the effect of the nitrate concentration on the $SrFe_{12}O_{19}$ contents in the products prepared in the presence of sulfates, experiments were carried out under the same conditions with those where the samples C2 and C6 had been obtained. Decreasing the nitrate concentration to 0.3 M did not affect the $SrFe_{12}O_{19}$ contents in the products obtained at 200 or

Table 3. The Typical Samples Prepared by Autoclaving at 200, 250 or 300°C Aqueous Suspensions Containing 0.45 M $FeSO_4$, 0.15 M $NaNO_3$, 0.11 M $Sr(NO_3)_2$ and Different Concentrations of Excess NaOH.

Samples	Excess NaOH/M	T/°C	M/emu g^{-1}	Hc/kOe
C1	3.0	300	42	0.9
C2	4.0	300	52	0.7
C3	5.0	300	46	0.5
C4	8.0	300	40	0.6
C5	4.0	250	56	0.6
C6	4.0	200	50	0.6

300°C, their M values being between 50 and 53 emu g^{-1}. With a further decrease in the concentration to 0.15 M, their M values decreased to 46 (at 300 °C) or 41 (at 200°C) emu g^{-1} as a result of an increase in the α-Fe_2O_3 content.

Similar experiments were carried out by decreasing the Sr(II) concentration to 0.08 M, under the same conditions with those for the samples C2 and C6. The M values of the $SrFe_{12}O_{19}$ samples prepared in the presence of 0.08 M Sr(II) were 52 emu g^{-1}. These results indicated that the presence of sulfates facilitated the formation of $SrFe_{12}O_{19}$ from $Fe(OH)_2$ in the strongly alkaline suspension.

The $SrFe_{12}O_{19}$ samples obtained in this work were found by SEM to consist of hexagonal, platelike particles (Figs. 1 and 2). Although some particles having a rodlike shape appear in the photographs, these were identified as platelike ones viewed in an edge-on orientation by tiling the sample station to about 40°. The photographs show that the growth for the (001) faces (basal

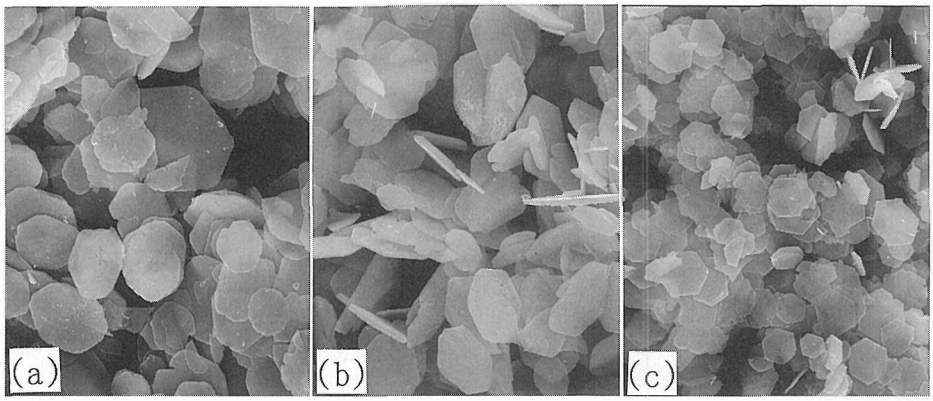

Fig. 1. SEM photographs of the typical $SrFe_{12}O_{19}$ samples A3 (a), B2 (b) and B4 (c) prepared in the absence of sulfates.

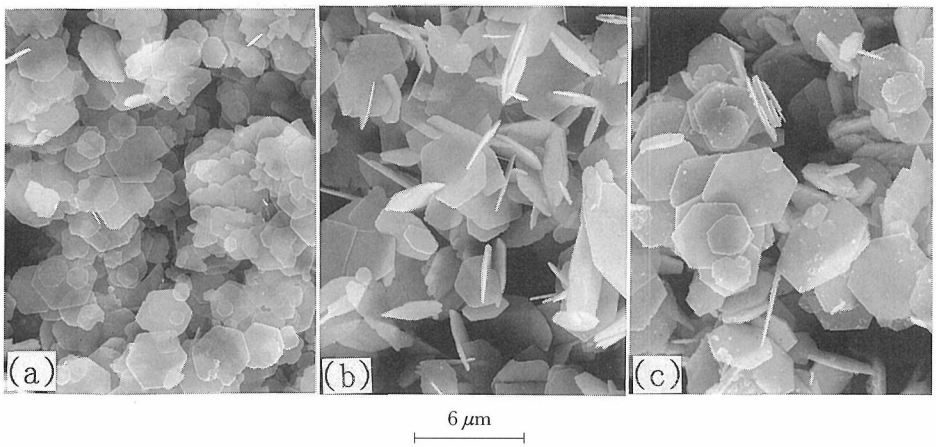

Fig. 2. SEM photographs of the typical $SrFe_{12}O_{19}$ samples C2 (a), C4 (b) and C6 (c) prepared in the presence of sulfates.

plane) of platelike $SrFe_{12}O_{19}$ particles by autoclaving is remarkably promoted in the presence of $Fe(OH)_2$ with nitrates. As shown above in each table, the Hc values of the products prepared from Fe(II) in the presence or absence of sulfates are remarkably lower than those of the ones prepared by a solid state reaction. Such low Hc values as below 1 kOe might have resulted from the extremely large sectional-shape anisotropy of each particle.

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